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(54) Heat shrinkable films containing single site catalyzed copolymers

Wärmeschrumpfbare, durch Single-site-Katalyse hergestellte Copolymeren enthaltende Folien.

Films rétractables à la chaleur contenant des copolymères catalisés par cataliseurs de site singulier

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chemical type rather than a volatile mixture of states as discussed for conventional Ziegler-Natta. This results in a system composed of catalyst positions which have a singular activity and selectivity. For this reason; metallocene catalyst systems are often referred to as "single site" owing to the homogeneous nature of them, and polymers and copolymers produced from them are often referred to as single site resins by their suppliers.

5 [0011] Generally speaking, metallocene catalysts are organometallic compounds containing one or more cyclopentadienyl ligands attached to metals such as hafnium, titanium, vanadium, or zirconium. A co-catalyst, such as but not limited to, oligomeric methyl alumoxane is often used to promote the catalytic activity. By varying the metal component and the cyclopentadienyl ligand a diversity of polymer products may be tailored having molecular weights ranging from about 200 to greater than 1,000,000 and molecular weight distributions from 1.5 to about 15. The choice of co-catalyst influences the efficiency and thus the production rate, yield, and cost.

10 [0012] Exxon Chemical, in U.S. Patent 4,701,432 sets out examples of which olefin catalyst systems are of the metallocene class and which are non-metallocene. They cite bis(cyclopentadienyl) dichloro-transition metal, bis(cyclopentadienyl) methyl, chloro-transition metal, and bis(cyclopentadienyl) dimethyl-transition metal as examples of metallocene catalysts, where the metals include choices such as titanium, zirconium, hafnium, and vanadium. The 15 patent further provides examples of non-metallocene catalysts as being $TiCl_4$, $TiBr_4$, $Ti(OC_4H_9)_2Cl_2$, VCl_4 , and $VOCl_3$.

15 [0013] Similarly, C.P. Cheng, at SPO 91, the Specialty Polyolefins Conference sponsored by Schotland and held in Houston, Texas in 1991, cited $TiCl_3/AlR_2Cl$ and $MgCl_2/TiCl_4/AlR_3$ as examples of non-metallocene Ziegler-Natta catalysts and transition metal cyclopentadienyl complexes as examples of metallocene homogeneous polyolefin catalysts.

20 [0014] As a consequence of the single site system afforded by metallocenes, ethylene/alpha-olefin copolymer resins can be produced with each polymer chain having virtually the same architecture. Therefore, the copolymer chains produced from single site systems are uniform not only in chain length, but also in average comonomer content, and even regularity of comonomer spacing, or incorporation along the chain.

25 [0015] In contrast to the above mentioned Ziegler-Natta polymers, these single site metallocene polymers are characterized as having a narrow MWD and narrow compositional distribution (CD). While conventional polymers have MWD's of about 3.5 to 8.0, metallocenes range in MWD from about 1.5 to about 2.5 and most typically about 2.0. MWD refers to the breadth of the distribution of molecular weights of the polymer chains, and is a value which is obtained by dividing the number-average molecular weight into the weight-average molecular weight. The low CD, or regularity of side branches chains along a single chain and its parity in the distribution and length of all other chains, greatly reduces the low MW and high MW "tails". These features reduce the extractables which arise from poor LMW control 30 as well as improve the optics by removing the linear, ethylene-rich portions which are present in conventional heterogeneous resins.

35 [0016] Thus, conventional Ziegler-Natta systems produce heterogeneous resins which reflect the differential character of their multiple catalyst sites while metallocene systems yield homogeneous resins which, in turn, reflect the character of their single catalytic site.

40 [0017] Another distinguishing property of single site catalyzed ethylene copolymers is manifested in their melting point range. The narrow CD of metallocenes produces a narrow melting point range as well as a lower Differential Scanning Calorimeter (DSC) peak melting point peak. Unlike conventional resins which retain a high-melting point over a wide density range, metallocene resin melting point is directly related to density. For example, an ethylene/butene copolymer having a density of 0.905 g/cc produced using a metallocene catalyst has a peak melting point of about 100°C, while a slightly lower density ethylene/butene copolymer which was made using a conventional Ziegler catalyst reflects its heterogeneous nature with a melting point at about 120°C. DSC shows that the Ziegler resin is associated with a much wider melting point range and actually melts higher despite its lower density.

45 [0018] In recent years several resin suppliers have been researching and developing metallocene catalyst technology. The following brief discussion should be viewed as representative rather than exhaustive of this active area of the patent literature.

50 [0019] Dow in EP 416,815 disclosed the preparation of ethylene/-olefin copolymers using monocyclopentadienylsilane complexed to a transition metal. The homogeneous ethylene copolymers which may be prepared using this catalyst are said to have better optical properties than typical ethylene polymers and be well suited for film or injection molding.

[0020] Welborn in Exxon U.S. 4,306,041 discloses the use of metallocene catalysts to produce ethylene copolymers which have narrow molecular weight distributions.

[0021] Chang, in Exxon U.S. 5,088,228 discloses the production of ethylene copolymers of 1-propene, 1-butene, 1-hexene, and 1-octene using metallocene catalysts.

[0022] Exxon in U.S. 4,935,397 discloses the production of ethylene copolymers using metallocene catalysts to manufacture polymer suitable for injection molding or thermoforming.

55 [0023] Welborn, in Exxon U.S. 5,084,534 discloses the use of bis(n-butylcyclopentadienyl) zirconium dichloride to produce high molecular weight polyethylene having a polydispersity of 1.8 and a density of 0.955 g/cm³.

[0024] In Exxon U.S. 3,161,629 a cyclopentadienyl complex is disclosed which may be used to produce polyolefins having controlled molecular weight and density suitable for use in extrusion or injection molding.

(200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.

[0040] Such objects are further achieved when the single site catalyzed copolymer is blended with another thermoplastic homopolymer or copolymer.

5 [0041] According to a further preferred embodiment of the present invention, the other thermoplastic homopolymer or copolymer is a heterogeneous polymer of ethylene and an alpha-olefin having from 3 to 10 carbon atoms. Said heterogeneous copolymer can have a density below about 0.90 g/cm³ or above about 0.90 g/cm³. Preferably, the other thermoplastic homopolymer or copolymer is a copolymer of ethylene and a second comonomer selected from the group consisting of vinyl acetate, alkyl acrylate, carbon monoxide, butadiene, styrene, acrylic acid and a metal-neutralized salt of an acrylic acid. Preferably, said thermoplastic polymer or copolymer is a homopolymer of an alpha-olefin, such as ethylene and an alpha-olefin having from 3 to 8 carbon atoms. Preferred embodiments of said homogeneous copolymers are a copolymer of ethylene and butene, a copolymer of ethylene and hexene or a copolymer of ethylene and octene.

10 [0042] According to a further preferred embodiment, the heat shrinkable film is a multilayer film and said homogeneous copolymer is present in at least one layer thereof, such as in an outer layer, which may be a heat sealing layer or in an inner layer.

15 [0043] The objects of the present invention are furthermore achieved by providing a heat shrinkable film having a substantially symmetrical structure comprising outer layers comprising a propylene homopolymer or copolymer, and a core layer comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin having from four to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5, wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.

20 [0044] Moreover, the objects of the present invention are achieved by providing a heat shrinkable, multi-layer film which includes a heat sealing layer, an inner layer comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5 and a barrier layer, and wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction. Preferably, said heat sealing layer comprises a copolymer of ethylene and a comonomer selected from the group consisting of vinyl acetate, alkyl acrylate, acrylic acid and a metal-neutralized salt of an acrylic acid, or a heterogeneous copolymer of ethylene and an alpha-olefin having from 3 to 10 carbon atoms, or a homogeneous single site catalyzed copolymer of ethylene and an alpha-olefin having from 3 to 10 carbon atoms.

25 [0045] Furthermore, the objects of the present invention are achieved by providing a heat shrinkable multi-layer film comprising a heat sealing layer comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5, and a barrier layer, wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.

30 [0046] The barrier layer referred to above preferably comprises a copolymer of vinylidene chloride and methyl acrylate, or a copolymer of vinylidene chloride and vinyl chloride, or an ethylene vinyl alcohol, or a nylon.

[0047] The multi-layer films of the present invention may include an outer abuse layer and/or at least one inner adhesive layer.

35 [0048] Moreover, the objects of the present invention are achieved by providing a heat shrinkable film comprising at least two layers wherein at least one of said layers comprises a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5, and wherein at least one of said layers is crosslinked and wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.

40 [0049] A further embodiment of the present invention relates to a heat shrinkable multi-layer film having a substantially symmetrical structure comprising outer layers comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5, and an inner core layer, wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction. Said inner core layer may comprise a copolymer of ethylene and a second comonomer selected from the group consisting of vinyl acetate, alkyl acrylate, acrylic acid and a metal-neutralized salt of an acrylic acid. Said multi-layer film

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of gas or moisture impermeability needed for the ultimate product to be packaged. Further internal layers may serve to add bulk to the film, promote shrinkability, promote interlayer adhesion or any combination of these properties.

5 [0058] The following examples are representative of the preferred embodiments of the present heat shrinkable films containing homogeneous linear ethylene alpha-olefin copolymers. In order to evaluate such films the following tests were employed:

Tensile Strength: A measure of the force required under constant elongation to break a specimen of the film; measured by ASTM D 882.

10 Elongation: A measure of the percent extension required to break a specimen of the film; measured by ASTM D 882.

15 Modulus: The ratio of the change in force to the change in elongation in the straight line portion of an Instron Tensile Testing curve; measured by ASTM D 882 - Method A.

15 Tear Propagation: The force required to propagate a tear from a tiny slit made by a sharp blade in a specimen of the film; measured by ASTM D 1938.

20 Free Shrink: The percent dimensional change in a 10 cm. x 10 cm. specimen of film when subjected to a selected heat; measured by ASTM D 2732.

25 Ball Burst: The energy necessary to burst and penetrate a restrained specimen of film; measured by ASTM D 3420.

30 Instrumented Impact: The energy necessary to puncture a restrained specimen of film, similar to ball burst, defined above. However, the Instrumented Impact Tester has the ability to measure the tensile/elongation curve to break. The "gradient" is the ratio of the change in force to change in elongation in the straight line portion of the curve. "Peak" is a measure of the maximum force exerted on the specimen to impart rupture. "Impact Energy" is a measure of the energy absorbed by the sample prior to rupture. Instrumented Impact is measured by ASTM D. 3763.

35 Haze: The percentage of transmitted light which is scattered forward while passing through a specimen; measured by ASTM D 1003 - Method A.

35 Clarity: A measure of the distortion of an image viewed through a specimen; measured by ASTM D 1746.

40 Gloss: The surface reflectance or shine of a specimen; measured by ASTM D 2457.

40 Parallel Plate: A bag is confined between two plates a specified distance apart and is inflated until its seal fails. The pressure level inside the bag at the point of failure is a measure of seal quality. Results are reported in meters (inches) of water pressure (MOWP) (IOWP)).

45 LRHB (Linear Ramped Hot Burst): A clean sealed bag is inflated to a specified dwell pressure and the seal area is submerged in hot water at 83°C (182 °F). After five seconds the pressure inside the bag is increased at the rate of 2 inches of water/second. The time to failure and burst pressure is a measure of seal quality. Test results are reported in seconds and meters (inches) of water pressure (MOWP) (IOWP)).

50 LRHB-G (Linear Ramped Hot Burst - Grease): The procedure is the same as the LRHB test described above except peanut oil is first applied to the seal area.

55 VPHB (Variable Pressure Hot Burst): As with the LRHB test described above, a clean sealed bag is inflated to a specified dwell pressure and the seal area is submerged in hot water at 83°C (182 °F). After five seconds the pressure inside the bag is increased at a specified rate ranging 1 to 7 inches of water/second. Here again, test results are reported as seconds and meters (inches) of water pressure (PCOWP) (IOWP)).

55 VPHB-G (Variable Pressure Hot Burst - Grease): The procedure is the same as the VPHB test described above except peanut oil is first applied to the seal area.

mm (1 mil).

Example 6

- 5 [0065] Two platens made from Fina 8473, an ethylene propylene copolymer (EPC) with 3.1% by weight ethylene were pressed in accordance with the film formation process set forth in Example 1. A third platen formed of Exxon SLP 3011A, a homogeneous ethylene hexene copolymer having a density of 0.910 g/cm³ and a 1.0 M.I. made by the process of Example 1 was placed between the two EPC platens. The three layers were then pressed under heat and pressure to weld the three into a single multilayer film.
- 10 [0066] The multilayer film was then oriented on the T.M. Longstretcher laboratory orientation unit at the University of Tennessee, Knoxville, Tennessee. The orientation conditions were as follows: air temperature = 105°C; dwell time = 30 sec.; stretch ratio = 4.0 x 4.0; strain ratio = 3900%; plate temperature = 105°C. The final film thickness was approximately 0.025 mm (1 mil).

15 Example 7 (Prior Art)

- [0067] As set forth in Example 6 above, a multilayer film was produced by pressing a platen of Exxon SLP 3011D (made by the process of Example 1) between two platens of ethylene propylene copolymer.
- 20 [0068] The film was oriented under the following conditions: air temperature = 100°C; dwell time = 30 sec.; stretch ratio = 4.0 x 4.0; strain ratio = 3900%; plate temperature = 100°C. The final film thickness was approximately 0.025 mm (1 mil).

Example 8 (Prior Art)

- 25 [0069] As set forth in Example 7 above, a multilayer film was produced by pressing a platen of Dowlex 2045 between two platens of ethylene propylene copolymer for comparative purposes.
- [0070] The film was oriented under the following condition: air temperature = 114.5°C; dwell time = 30 sec.; stretch ratio = 4.0 x 4.0; strain ratio = 3900%; plate temperature = 115°C. The final film thickness was approximately 0.025 mm (1 mil).

30 Example 9

- 35 [0071] Several physical properties of the oriented monolayer film samples of Example 1 - 5 were evaluated and are given below in Table 1. The film of Example 5 is representative of the prior art and is given for comparative purposes.

Table 1

Property/	Film of				
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 5
Tensile, (psi) MPa	(15,300) 105.49	(22,917) 158.01	(19,088) 131.61	(18,822) 129.77	(13,500) 93.079
Elongation, %	142	160	201	175	181
Modulus, MPa (psi)	186.16 (27,000)	113.79 (16,504)	93.093 (13,502)	102.81 (14,912)	317.16 (46,000)
Tear Propogation grams	88	10	87	54	110
Free Shrink, % (at 93 °C (200°F))	13/10	43/38	50/48	55/53	3/6
Ball Burst cm - kg	11.0	45	50+	50+	5.3
Instrumented Impact	15.0	31	65	60	5.0
Haze, %	5.9	0.5	1.0	1.4	2.7
Clarity, %	44	89	81	83	80
Gloss, 45 deg.	65	95	89	88	77

[0072] The numbers shown for tear propogation for each film are subject to a very high standard deviation.

Table III

<u>Example</u>	<u>Dose</u>	<u>Preheat</u>	<u>Hotbath</u>	<u>Core</u>
11	2MR	195	195	SLP 3011D
12	4MR	195	195	SLP 3011D
13	2MR	210	210	SLP 3011D
14	4MR	210	210	SLP 3011D
15	2MR	195	195	SLP 3011B
16	4MR	195	195	SLP 3011B
17	2MR	210	210	SLP 3011B
18	4MR	210	210	SLP 3011B
19	2MR	195	195	Attane 4203
20	4MR	195	195	Attane 4203
21	2MR	210	210	Attane 4203
22	4MR	210	210	Attane 4203

[0078] Exxon SLP 3011B is a homogeneous ethylene hexene copolymer having a density of 0.905 g/cm³ and a 2.1 M.I. Attane 4203 is a heterogeneous ethylene octene copolymer having a density of 0.905 g/cm³.

[0079] The oriented multilayer films of Examples 11-22 were tested for free shrink and instrumented impact with the results given below in Table IV. It may be seen that when comparing the metallocene resin films of Examples 11 and 15 or 12 and 16 with the comparative example counterparts of 19 and 20, a substantial improvement in impact resistance is seen. Similarly, a comparison of Examples 13 and 17 or 14 and 18 with their respective comparative heterogeneous Examples 21 and 22 show an improved impact for the metallocene resins.

Table IV

Ex. #	Free Shrink			Instrumented Impact		
	L	T	Peak	Grad	Energy	
			kg (lbs.)	N/m (lb/in.)	Nm (ft.lb)	
11	31	45	29.4(86.8)	9965(56.9)	2.03(5.97)	
12	31	45	39.0(86.0)	9667(55.2)	2.22(6.06)	
13	14	34	16.3(87.1)	5714(33.2)	2.65(1.96)	
14	17	34	21.0(46.4)	5267(33.5)	3.71(2.74)	
15	30	41	35.1(77.4)	9369(53.5)	7.24(5.34)	
16	30	42	32.6(71.9)	9037(51.6)	5.58(4.12)	
17	17	35	19.7(43.5)	6515(37.2)	3.70(2.73)	
18	18	34	25.4(56.4)	6637(37.9)	5.65(4.17)	
19	30	45	24.6(54.2)	8056(46.0)	3.95(2.91)	
20	30	45	25.0(55.1)	8651(49.4)	3.57(2.63)	
21	20	37	18.6(40.9)	6585(7.6)	2.64(1.95)	
22	21	38	20.1(46.1)	7145(40.8)	2.98(2.20)	

Table V

5	Ex. #	Film of	A	Parallel Plate	VPHB	VPHB-G
	27	23	6.0	123.3	7.4	4.6
10	28	23	7.5	120.8	13.4	10.7
	29	23	9.0	144.8	13.3	12.6
15	30	24	6.0	138.6	0	7.6
	31	24	7.5	143.4	14.1	10.7
20	32	24	9.0	140.9	15.5	13.2
	33	25	6.0	138.0	24.5	22.9
	34	25	7.5	148.0	31.1	32.6
25	35	25	9.0	147.7	33.1	33.4
	36	26	6.0	146.9	20.4	14.5
	37	Comp. 26	7.5	145.9	21.7	19.7
30	38	26	9.0	159.0	23.4	22.9

Example 39

[0087] A two layer coextruded precursor film was formed having an inner layer of Exxon SLP 9017 a homogeneous ethylene hexene copolymer having a density of 0.920 g/cm³ and a 3.0 M.I. and an outermost layer of Excorene LD 720.92 from Exxon, EVA-1.

[0088] Following irradiation the precursor film was extrusion coated with a first barrier layer of a vinylidene chloride methyl acrylate supplied by Dow, a second layer of EVA-1 and an abuse layer of LD 318.92 from Exxon, EVA-2. The film structure was then oriented out of hot water by a trapped bubble technique. The final overall structure and target percent thickness per layer was:

SLP 9017/EVA-1/Saran/EVA-1/EVA-2
14.58% 50.42% 10% 12.5% 12.5%

Example 40

[0089] The procedure set forth in Example 39 was repeated with the exception that the inner layer of the precursor film was formed of a blend of 90% by weight of Exxon SLP 9017 and 10% by weight of Exxon SLP 4008, a homogeneous ethylene hexene copolymer having a density of 0.885 g/cm³ and a 4 M.I.

Example 41

[0090] The procedure set forth in Example 39 was repeated with the exception that the inner layer of the precursor film was formed of a blend of 80% by weight of Exxon SLP 9017 and 20% by weight Exxon SLP 4008.

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copolymer having a density of 0.910 and a 1.0 M.I. substantially as described by the film forming process of Example 1 above. One platen was not irradiated while the other three were irradiated to dosages of 3 MR, 4.5 MR and 7 MR respectively. Thereafter, each platen was oriented on the T.M. Long Stretcher substantially as described in the orientation procedure of Example 1 above. Each platen was oriented at 92°C. Thereafter, the resultant oriented films were measured for percent gel and instrumented impact at peak load and energy to break. The results are detailed in Table VII below.

Table VII

EX#	MR	%GEL	INSTRUMENTED IMPACT Peak (kg (lb))
58	0	0	17.2 (38)
59	3	0	21.3 (47)
60	4.5	32.7	19.0 (42)
61	7	56.0	17.7 (39)

Examples 62-65

[0100] Four monolayer platens were pressed from samples of Exxon SLP 3011D by the procedure set forth above for Examples 58-61. However, each platen was oriented at 85°C. Test results are shown in Table VIII below.

Table VIII

EX#	MR	%GEL	INSTRUMENTED IMPACT Peak (kg (lb))
62	0	0	18.1 (40)
63	3	0	17.7 (39)
64	4.5	23.2	19.1 (42)
65	7	56.0	21.3 (47)

Examples 66-73

[0101] The films of Examples 58 - 65 above were tested to determine tensile strength elongation and modulus in both the transverse and longitudinal directions. The results are given in Table IX below.

Table IX

Ex#	Film of Ex.#	Tensile (MPa (psi)) L/T	Elongation (%) L/T	Modulus x 1000 (MPa (psi)) L/T
66	58	106 / 134 (15400/19500)	115/215	0.150 / 0.203 (21.9/29.5)
67	59	119 / 122 (17300/17700)	120/200	0.170 / 0.121 (24.7/17.5)
68	60	112 / 141 (16200/20400)	105/270	0.172 / 0.186 (24.9/27.0)
69	61	162 / 110 (23500/16000)	150/150	0.119 / 0.199 (17.2/28.8)
70	62	102 / 103 (14800/15000)	160/210	0.077 / 0.107 (11.1/15.5)
71	63	139 / 69.6 (20200/10100)	160/180	0.730 / 0.986 (10.6/14.3)
72	64	121 / 84.1 (17500/12200)	140/180	0.917 / 0.058 (13.3/8.4)
73	65	103 / 89.6 (15000/13000)	140/190	0.071 / 0.88 (10.3/12.7)

Example 74

[0102] A two layer coextruded precursor film was formed having an inner layer of LD 318.92 from Exxon, EVA-1, and a second layer of Exxon SLP 3010D, a homogeneous ethylene butene copolymer having a density of 0.902 and a 1.0 M.I. The precursor film was irradiated at a dosage of 4.5 MR.

[0103] Thereafter, the precursor film was extrusion coated with a barrier layer of a vinylidene chloride methyl acrylate supplied by Dow, and then a layer of EP 4062-3 an ethylene vinyl acetate having 15% vinyl acetate EVA-2 and an abuse layer of EVA-1.

[0104] The total structure was oriented out of hot water with a preheat temperature of 195°C and a hot bath temperature of 188°C. The resultant oriented film had a structure and percent thickness per layer as follows:

EVA-1/SLP 3011D//Saran/EVA-2/EVA-1
14.29% 51.43% 9.80 16.33% 8.16

Example 83

[0112] The procedure of Example 81 was repeated with the exception that the skin layers A were a blend of 84% by weight of Exxon SLP 0233, a homogeneous ethylene hexene copolymer having a density of 0.922 and 16% by weight of Attane 4202, a heterogeneous ethylene octene copolymer having a density of 0.912 g/cm³.

[0113] The foregoing description of preferred embodiments of the invention have been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in light of the above teachings or may be acquired from practice of the invention. The embodiment were chosen and described in order to explain the principles of the invention and its practical application to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto, and their equivalents.

15 **Claims**

1. A heat shrinkable film comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5, said film having a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.
2. A heat shrinkable film as set forth in claim 1, wherein said single site catalyzed copolymer is blended with another thermoplastic homopolymer or copolymer.
3. A heat shrinkable film as set forth in claim 2, wherein said other thermoplastic homopolymer or copolymer is a heterogeneous polymer of ethylene and an alpha-olefin having from three to ten carbon atoms.
4. A heat shrinkable film as set forth in claim 3 wherein said heterogeneous copolymer has a density below 0.90 g/cm³.
5. A heat shrinkable film as set forth in claim 3 wherein said heterogeneous copolymer has a density above 0.90 g/cm³.
6. A heat shrinkable film as set forth in claim 2, wherein said other thermoplastic homopolymer or copolymer is a copolymer of ethylene and a second comonomer selected from the group consisting of vinyl acetate, alkyl acrylate, carbon monoxide, butadiene, styrene, acrylic acid, and a metal neutralized salt of an acrylic acid.
7. A heat shrinkable film as set forth in claim 2, wherein said thermoplastic homopolymer or copolymer is a homopolymer of an alpha-olefin.
8. A heat shrinkable film as set forth in claim 2, wherein said other copolymer is a copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms.
9. A heat shrinkable thermoplastic film as set forth in claim 8 wherein said homogeneous copolymer is a copolymer of ethylene and butene, or a copolymer of ethylene and hexene, or a copolymer of ethylene and octene.
10. A heat shrinkable film as set forth in claims 1 to 9, wherein said film is a multilayer film and said homogeneous copolymer is present in at least one layer of said multilayer film.
11. A heat shrinkable film as set forth in claim 10, wherein said homogeneous copolymer is present in an outer layer.
12. A heat shrinkable film as set forth in claim 11, wherein said outer layer is a heat sealing layer.
13. A heat shrinkable film as set forth in claim 10, wherein said homogeneous copolymer is present in an inner layer.
14. A heat shrinkable film having a substantially symmetrical structure comprising:
outer layers comprising a propylene homopolymer or copolymer; and
a core layer comprising a homogeneous linear single site catalyzed copolymer of ethylene and an alpha-olefin

having from three to eight carbon atoms, said copolymer having a density of at least 0.90 g/cm³ and a molecular weight distribution of from 1.5 to 2.5;

and an inner core layer,

wherein said film has a free shrink as the percent dimensional change in a 10 cm x 10 cm specimen of film when subjected to a heat of 93°C (200°F) measured by ASTM D 2732 of at least 10 percent in the transversal direction and 13% in the longitudinal direction.

24. A heat shrinkable multilayer film as set forth in claim 23, wherein said inner core layer comprises a copolymer of ethylene and a second comonomer selected from the group consisting of vinyl acetate, alkyl acrylate, acrylic acid, and a metal neutralized salt of an acrylic acid.
25. A heat shrinkable multilayer film as set forth in claim 23 and 24 further including two substantially identical inner layers immediately adjacent opposed surfaces of said inner core layer.
26. A heat shrinkable multilayer film as set forth in claim 25, wherein said inner layers comprise a heterogeneous copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms, or a homogeneous single site catalyzed copolymer of ethylene and an alpha-olefin having from three to eight carbon atoms.
27. A heat shrinkable multilayer film as set forth claims 23 to 26, wherein said outer layers include at least one further heterogeneous copolymer of ethylene and an alpha-olefin having from three to ten carbon atoms.

Patentansprüche

1. Wärmeschrumpfbare Folie, umfassend ein homogenes lineares Single-Site-katalysiertes Copolymer aus Ethylen und einem alpha-Olefin mit drei bis zehn Kohlenstoffatomen, wobei das Copolymer eine Dichte von mindestens 0,90 g/cm³ und eine Molekulargewichtsverteilung von 1,5 bis 2,5 aufweist, wobei die Folie eine freie Schrumpfung als prozentuale Dimensionsänderung in einem 10 cm x 10 cm-Teststück der Folie von mindestens 10% in der Querrichtung und 13% in der Längsrichtung aufweist, wenn sie einer Wärme von 93°C (200°F) ausgesetzt wird, gemessen nach ASTM D 2732.
2. Wärmeschrumpfbare Folie nach Anspruch 1, worin das Single-Site-katalysierte Copolymer mit einem weiteren thermoplastischen Homopolymer oder Copolymer gemischt ist.
3. Wärmeschrumpfbare Folie nach Anspruch 2, worin das andere thermoplastische Homopolymer oder Copolymer ein heterogenes Polymer aus Ethylen und einem alpha-Olefin mit drei bis zehn Kohlenstoffatomen ist.
4. Wärmeschrumpfbare Folie nach Anspruch 3, worin das heterogene Copolymer eine Dichte unterhalb von 0,90 g/cm³ aufweist.
5. Wärmeschrumpfbare Folie nach Anspruch 3, worin das heterogene Copolymer eine Dichte oberhalb von 0,90 g/cm³ aufweist.
6. Wärmeschrumpfbare Folie nach Anspruch 2, worin das andere thermoplastische Homopolymer oder Copolymer ein Copolymer aus Ethylen und einem zweiten Comonomer, ausgewählt aus der Gruppe, bestehend aus Vinylacetat, Alkylacrylat, Kohlenmonoxid, Butadien, Styrol, Acrylsäure, und einem Metall-neutralisierten Salz einer Acrylsäure, darstellt.
7. Wärmeschrumpfbare Folie nach Anspruch 2, worin das thermoplastische Homopolymer oder Copolymer ein Homopolymer eines alpha-Olefins darstellt.
8. Wärmeschrumpfbare Folie nach Anspruch 2, worin das andere Copolymer ein Copolymer aus Ethylen und einem alpha-Olefin mit drei bis acht Kohlenstoffatomen ist.
9. Wärmeschrumpfbare thermoplastische Folie nach Anspruch 8, worin das homogene Copolymer ein Copolymer aus Ethylen und Buten oder ein Copolymer aus Ethylen und Hexen oder ein Copolymer aus Ethylen und Octen ist.

21. Wärmeschrumpfbare Multischichtfolie nach einem der Ansprüche 16 bis 20, welche weiterhin mindestens eine innere Haftschiicht umfasst.

5 22. Wärmeschrumpfbare Folie, umfassend mindestens zwei Schichten, wobei mindestens eine der Schichten ein homogenes lineares Single-Site-katalysiertes Copolymer aus Ethylen und einem alpha-Olefin-Copolymer aus Ethylen und einem alpha-Olefin mit drei bis acht Kohlenstoffatomen umfasst, wobei das Copolymer eine Dichte von mindestens 0.90 g/cm³ und eine Molekulargewichtsverteilung von 1,5 bis 2,5 aufweist, und worin mindestens eine der Schichten vernetzt ist und worin die Folie eine freie Schrumpfung als die prozentuale Dimensionsänderung in einem 10 cm x 10 cm-Teststück der Folie von mindestens 10% in der Querrichtung und 13% in der Längsrichtung aufweist, wenn sie einer Wärme von 93°C (200°F) ausgesetzt wird, gemessen nach ASTM D 2732.

10 23. Wärmeschrumpfbare Multischichtfolie mit einer im Wesentlichen symmetrischen Struktur, umfassend:

15 äußere Schichten, umfassend ein homogenes lineares Single-Site-katalysiertes Copolymer aus Ethylen und einem alpha-Olefin mit drei bis acht Kohlenstoffatomen, wobei das Copolymer eine Dichte von mindestens 0.90 g/cm³ und eine Molekulargewichtsverteilung von 1,5 bis 2,5 aufweist; und eine innere Kernschicht,

20 worin die Folie eine freie Schrumpfung als die prozentuale Dimensionsänderung in einem 10 cm x 10 cm-Teststück der Folie von mindestens 10% in der Querrichtung und 13% in der Längsrichtung aufweist, wenn sie einer Wärme von 93°C (200°F) ausgesetzt wird, gemessen nach ASTM D 2732.

25 24. Wärmeschrumpfbare Multischichtfolie nach Anspruch 23, worin die innere Kernschicht ein Copolymer aus Ethylen und einem zweiten Comonomer, ausgewählt aus der Gruppe, bestehend aus Vinylacetat, Alkylacrylat, Acrylsäure, und einem Metall-neutralisierten Salz einer Acrylsäure, umfasst.

30 25. Wärmeschrumpfbare Multischichtfolie nach Ansprüchen 23 und 24, welche weiterhin zwei im Wesentlichen identische innere Schichten umfasst, welche den entgegengesetzten Oberflächen der inneren Kernschicht direkt benachbart sind.

35 26. Wärmeschrumpfbare Multischichtfolie nach Anspruch 25, worin die inneren Schichten ein heterogenes Copolymer aus Ethylen und einem alpha-Olefin mit drei bis zehn Kohlenstoffatomen oder ein homogenes Single-Site-katalysiertes Copolymer aus Ethylen und einem alpha-Olefin mit drei bis acht Kohlenstoffatomen umfasst.

40 27. Wärmeschrumpfbare Multischichtfolie nach einem Ansprüchen 23 bis 26, worin die äußeren Schichten mindestens ein weiteres heterogenes Copolymer aus Ethylen und einem alpha-Olefin mit drei bis zehn Kohlenstoffatomen umfassen.

45 **Revendications**

1. Film thermorétractable comprenant un copolymère linéaire homogène obtenu par catalyse mono-site d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone, ledit copolymère ayant une densité d'au moins 0,90 g/cm³ et une répartition des masses moléculaires comprise entre 1,5 et 2,5, ledit film ayant un retrait libre comme changement dimensionnel en pourcentage dans un échantillon de film de 10 cm x 10 cm lorsqu'il est soumis à une chaleur de 93 °C (200 °F) mesurée selon la norme ASTM D 2732 d'au moins 10 pour cent dans la direction transversale et 13 % dans la direction longitudinale.

50 2. Film thermorétractable selon la revendication 1, dans lequel ledit copolymère obtenu par catalyse mono-site est mélangé à un autre copolymère ou homopolymère thermoplastique.

3. Film thermorétractable selon la revendication 2, dans lequel ledit autre copolymère ou homopolymère thermoplastique est un polymère hétérogène d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone.

55 4. Film thermorétractable selon la revendication 3, dans lequel ledit copolymère hétérogène a une densité inférieure à 0,90 g/cm³.

5. Film thermorétractable selon la revendication 3, dans lequel ledit copolymère hétérogène a une densité supérieure

l'acrylate d'alkyle, l'acide acrylique, et un sel métallique d'un acide acrylique neutralisé, ou un copolymère hétérogène d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone, ou un copolymère homogène obtenu par catalyse mono-site d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone.

5 18. Film multicouches thermorétractable comprenant :

une couche thermosoudable comprenant un copolymère linéaire homogène obtenu par catalyse mono-site d'éthylène et d'une alpha-oléfine ayant trois à huit atomes de carbone, ledit copolymère ayant une densité d'au moins 0,90 g/cm³ et une répartition des masses moléculaires comprise entre 1,5 et 2,5 ;
10 et une couche barrière,

dans lequel ledit film a un retrait libre comme changement dimensionnel en pourcentage dans un échantillon de film de 10 cm x 10 cm lorsqu'il est soumis à une chaleur de 93 °C (200 °F) mesurée selon la norme ASTM D'2732 d'au moins 10 pour cent dans la direction transversale et 13 % dans la direction longitudinale.

15 19. Film multicouches thermorétractable selon la revendication 16 ou 18, dans lequel ladite couche barrière comprend un copolymère de chlorure de vinylidène et d'acrylate de méthyle, ou un copolymère de chlorure de vinylidène et de chlorure de vinyle, ou un alcool de vinyle d'éthylène, ou un nylon.

20 20. Film multicouches thermorétractable selon les revendications 16 à 19, incluant une couche d'usure extérieure.

21. Film multicouches thermorétractable selon les revendications 16 à 20, incluant en outre au moins une couche adhésive intérieure.

25 22. Film thermorétractable comprenant au moins deux couches dans lequel au moins une desdites couches comprend un copolymère linéaire homogène obtenu par catalyse mono-site d'éthylène et d'un copolymère d'alpha-oléfine d'éthylène et une alpha-oléfine ayant trois à huit atomes de carbone, ledit copolymère ayant une densité d'au moins 0,90 g/cm³ et une répartition des masses moléculaires comprise entre 1,5 et 2,5, et dans lequel au moins une desdites couches est réticulée et dans lequel ledit film a un retrait libre comme changement dimensionnel en pourcentage dans un échantillon de film de 10 cm x 10 cm lorsqu'il est soumis à une chaleur de 93 °C (200 °F) mesurée selon la norme ASTM D 2732 d'au moins 10 pour cent dans la direction transversale et 13 % dans la direction longitudinale.

35 23. Film multicouches thermorétractable ayant une structure sensiblement symétrique comprenant :

des couches extérieures comprenant un copolymère linéaire homogène obtenu par catalyse mono-site d'éthylène et d'une alpha-oléfine ayant trois à huit atomes de carbone, ledit copolymère ayant une densité d'au moins 0,90 g/cm³ et une répartition des masses moléculaires comprise entre 1,5 et 2,5 ;
40 et une couche centrale intérieure,

dans lequel ledit film a un retrait libre comme changement dimensionnel en pourcentage dans un échantillon de film de 10 cm x 10 cm lorsqu'il est soumis à une chaleur de 93 °C (200 °F) mesurée selon la norme ASTM D 2732 d'au moins 10 pour cent dans la direction transversale et 13 % dans la direction longitudinale.

45 24. Film multicouches thermorétractable selon la revendication 23, dans lequel ladite couche centrale intérieure comprend un copolymère d'éthylène et un second comonomère sélectionné dans le groupe consistant en l'acétate de vinyle, l'acrylate d'alkyle, l'acide acrylique, et un sel métallique d'un acide acrylique neutralisé.

50 25. Film multicouches thermorétractable selon les revendications 23 et 24 incluant en outre deux couches intérieures sensiblement identiques immédiatement adjacentes à des surfaces opposées de ladite couche centrale intérieure.

55 26. Film multicouches thermorétractable selon la revendication 25, dans lequel lesdites couches intérieures comprennent un copolymère hétérogène d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone, ou un copolymère obtenu par catalyse mono-site homogène d'éthylène et d'une alpha-oléfine ayant trois à huit atomes de carbone.

27. Film multicouches thermorétractable selon les revendications 23 à 26, dans lequel lesdites couches extérieures comprennent au moins un autre copolymère hétérogène d'éthylène et d'une alpha-oléfine ayant trois à dix atomes de carbone.